Structures and properties evolution with size of ScN nanocrystals: A first-principles study

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Abstract

The lowest-energy structures and properties evolution with the size of Sc₄N₄ₙ nanocrystals (n = 3–54) are explored by first-principles calculations. The formation of cage-like Sc₄N₄ₙ units is energetically favorable. In small-size nanocrystals, the Sc₄N₄ₙ units prefer to arrange into the rectangular-like wire structures, whereas they arrange into the compact rectangular-like or cubic-like configurations in large-size nanocrystals. The Sc₄N₄ₙ cage can be viewed as the embryo of ScN bulk crystal. With the obtained lowest-energy structures, we calculated some physical properties such as binding energies, HOMO–LUMO gaps, ionization potentials, and electron affinities. The evolution of these properties with the size was discussed.

1. Introduction

Group III nitrides, especially GaN, are widely used in the micro- and optoelectronic devices [1] and have been attracting the growing interest in both fundamental studies and technological applications [2]. Recently, several experimental and theoretical studies are performed to reveal the atomic and electronic structures of ScN thin films and bulk crystals [3–10]. ScN, a group III nitride, exhibits the extraordinary physical properties of high hardness and high-temperature stability. The small lattice misfit between ScN and cubic GaN provides the possibility of combining ScN and GaN to form ScN/GaN heterojunctions [11] or ScGaN alloys [12,13]. These make the ScN one promising complementary material to well-known AlN, GaN, and InN group III nitrides. Besides the exploration of ScN thin films and bulk crystals, there are a few experimental and theoretical investigations on the electronic and vibrational properties of ScN molecules [14–20]. However, less attention is given to the medium-sized ScN nanocrystals. The characteristic evolution with the size of ScN from diatomic molecules to bulk crystals is of key importance to understand the growth mechanism of ScN nanocrystals and thin films and use the ScN nanostructures in functional nanodevices.

In the previous density functional theory (DFT) studies on stoichiometric BN, AlN, and GaN clusters, crossovers from ring to cage-like structures were found to occur as the cluster size increases [21–23]. For BₙNₙ clusters, the ring-to-cage crossover occurs at the critical size of n = 11 [21]. The AlₙNₙ cage is more stable than the ring [22]. For GaₙNₙ clusters, the size for the ring-to-cage crossover is n = 8 between BN (n = 11) and AlN (n = 6) [23]. The cage-like configurations in medium size GaN clusters were observed to involve six-membered rings with the Ga–N alternative arrangement, which was suggested as the embryo of wurtzite structure of gallium nitride crystal.

In this Letter, we report first-principles DFT calculations about the stable structures and properties evolution with the size of ScN clusters and nanocrystals. The Sc and N atoms in ScN clusters tend to maximize the number of Sc–N bonds and form the compact nonplanar structures. The Sc₄N₄ cage is more stable than the ring, indicating the crossover from ring to cage occurs as early as n = 4 for Sc₄N₄ clusters. The formation of cage-like Sc₄N₄ units is preferred in medium-sized clusters. The cubic-like Sc₄N₄ cage can be viewed as the embryo of the ScN nanoparticles and bulk crystal. With these observations, the Sc₂₅N₂₅ nanocrystals (n = 3–54) are concentrated onto reveal the structures and properties evolution with the size. The Sc and N atoms in these nanocrystals prefer the Sc–N alternative arrangement. The formation of cage-like Sc₄N₄ units is energetically favorable. The Sc₄N₄ units prefer to arrange into the rectangular-like wire structures in small-size nanocrystals, whereas they arrange into the compact rectangular-like or cubic-like configurations in large-size nanocrystals. After obtaining the lowest-energy structures, we calculated their binding energies, vibrational spectra, and electronic properties. The evolution of these properties with the nanocrystal size was discussed.

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2. Computational details

The calculations were conducted in the framework of DFT method with Dmol package [24]. We used the exchange–correlation functional parameterized by Perdew, Burke, and Ernzerhof (PBE) in the generalized-gradient Approximation (GGA) [25]. A double numeric basis set including p-polarization function (DNP) and all electrons treatment were employed to carry out the geometry optimization, vibrational frequency, and electronic structure calculations. Spin unrestricted self-consistent field calculations were performed with a convergence energy of 1.0 × 10⁻⁵ Hartree (1 Hartree = 27.2114 eV) for total energies. In order to verify the reliability and accuracy of DFT/PBE method, the bond length and harmonic frequency of ScN molecule were calculated and compared with the previous experimental observations and theoretical calculations. The computed bond length of 1.679 Å agrees well with the reported value of 1.678 Å [16]. The harmonic frequency of 880.1 cm⁻¹ obtained in the present work is slightly less than the reported value of 930.0 cm⁻¹ [16]. Thus, the DFT/PBE method can be used to study the structures and properties of ScN nanocrystals.

Starting with a large number of possible structural isomers of ScN clusters and nanocrystals which are constructed by considering the structures from the literatures for BN, AlN and GaN clusters [21–23,26–35], the geometry optimization was conducted to search for the lowest-energy structures. We also constructed ScN clusters following some structural rules. For example, the Sc₄N₄ cages are preferred as the building blocks in medium-sized clusters. In order to ensure the computed structures corresponding to the true minima on the potential energy surface (PES), the vibrational frequencies were calculated and analyzed. The structures with the imaginary frequencies are unstable and may correspond to the saddle points on the PES. Based on the lowest-energy structures, we calculated and discussed the size-dependent evolution of some physical properties of ScN nanocrystals.

3. Results and discussion

Figure 1 shows the lowest-energy configurations of ScₙNₘ clusters (n = 3–5, m = 5). It is found that these clusters tend to maximize the number of Sc–N bonds and prefer the Sc–N alternative arrangement. This tendency may be related to the repulsive interaction between the lone-pair electrons on N atoms. According to the valence shell electron pair repulsion theory [36], N atom has five valence electrons and Sc is trivalent. When the Sc–N bond is formed, two valence electrons are left on the N atoms, which are called as the lone-pair electrons. The clusters can minimize the repulsive interaction between the lone-pair electrons on N atoms by the Sc–N alternative arrangement. We also observed that it is energetically favorable for the formation of the cubic-like Sc₄N₄ units in medium-sized clusters. The ScN bulk crystal exhibits the cubic rock-salt structure. The cubic-like Sc₄N₄ cage can be viewed as the embryo of the ScN nanoparticles and bulk crystal. For medium-sized GaN clusters, it was reported that the formation of six-membered rings (6MRs) is energetically favorable [23]. Ga₉N₉ cluster consists of two interlaced 6MRs. Larger Ga₇N₇, Ga₈N₈, Ga₉N₉, Ga₁₀N₁₀, Ga₁₁N₁₁, Ga₁₂N₁₂ cage-like clusters involve three, four, five, four, seven, and eight 6MRs. As the wurtzite structure of GaN crystal can be constructed by the same type of Ga–N 6MRs, the cage-like GaN clusters were suggested as the embryo of GaN bulk crystal [23].

Based on the observation of the preferred bonding configurations in ScN clusters, we concentrate on the study of lowest-energy geometries, energetic stabilities, vibrational frequencies, and electronic properties of ScₙNₘ nanocrystals (n = 3–54). Figure 2 shows the lowest-energy configurations of the considered nanocrystals and Figure 3 shows some typical low-energy structures. The most stable Sc₄N₄ structure has the rectangular-like wire geometry with two cubic-like cages. The hexagonal-ring Sc₆N₆ structure is higher in energy at 0.9 eV (see Figure 3a). This observation is different from Ga₉N₉, which has the hexagonal-ring lowest energy isomer [23]. The most stable Sc₉N₉ and Sc₁₀N₁₀ nanocrystals also have the rectangular-like wire geometries with three and four cubic-like cages, respectively. The total energy increases by 1.0 eV for Sc₁₀N₁₀ as it consists of one hexagonal-ring cage and one cubic-like cage.
For Sc10N10, the isomer composed by two hexagonal-ring cages has the higher energy at 1.9 eV. For Sc12N12 nanocrystal, the rectangular-like wire structure becomes less stable. The lowest-energy structure exhibits the rectangular-like compact geometry with the cages arranged parallelly, as shown in Figure 2d. The double-hexagonal-ring Sc12N12 structure is 3.2 eV higher in energy. The most stable Sc16N16 and Sc24N24 structures are compact rectangular-like with the parallel cubic-like cages (see Figure 2e and f). The most stable Sc32N32 and Sc108N108 nanocrystals exhibit the cubic-like configurations.

The lowest-energy structure of ScN nanocrystals obtained in the present work may not correspond to the global minima on the PES. However, the trend for the structural evolution of nanocrystals with the size can be identified, which would not strongly depend on the details of the PES. The calculated results indicate that the nanocrystals prefer to form the cubic-like Sc4N4 cages and the cages tend to arrange into the compact configurations with the increasing nanocrystal size.
Correspond to the true minima on PES. Figure 4 shows the representative vibrational spectra of the Sc4N4, Sc12N12, and Sc108N108 nanocrystals. These vibrational modes reflect the assigned movements of the Sc–N bonds. The low lying frequencies are assigned to the Sc–N bending modes, whereas the vibrational modes around 600 cm⁻¹ correspond to either symmetric or asymmetric stretching modes of Sc–N bonds.

To study the electron structure evolution with size of ScN nanocrystals, we calculated the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the above lowest-energy structures. Figure 5 shows the size dependence of HOMO level, LUMO level, and HOMO–LUMO gaps of Sc2nN2n nanocrystals (n = 2–6, 8, 12, 18, 54). A decreasing trend is observed in the gap values with the increasing nanocrystal size. Figure 6 shows the HOMOs and LUMOs of Sc6N6, and Sc32N32 nanocrystals. The HOMO of Sc6N6 is characterized by the delocalization of the sites of outside Sc atoms. The HOMO of Sc32N32 nanocrystal is mainly localized on the sites of N atoms and the LUMO is distributed around Sc atoms with a delocalized character in the central region.

The size-dependence of some other physical properties of ScN nanocrystals is computed and collected in Table 1. The binding energies increase with the increasing nanocrystal size and approaches gradually towards the bulk value. A decreasing trend is observed for the ionization potentials. The electron affinities are negative for small-size nanocrystals and positive for larger nanocrystals. The HOMO–LUMO gaps exhibit a decreasing trend with the increasing size, indicating the promoted electronic stability with the reduced nanocrystal size. The theoretical predications can be verified by future experiments.

**4. Conclusions**

The lowest-energy structures, vibrational frequencies, and electronic properties of Sc2nN2n nanocrystals are studied with first-principles DFT calculations. It is found that the Sc and N atoms in these nanocrystals prefer the Sc–N alternative arrangement. The formation of cage-like Sc2N4 units is energetically favorable. In small-size nanocrystals, the Sc2N4 units prefer to arrange into the rectangular-like wire structures, whereas they arrange into the compact rectangular-like or cubic-like configurations in large-size nanocrystals. With the obtained lowest-energy structures, we calculated and discussed their properties evolution with the size.

## Table 1

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